Effect of the molecular weight on the static electro-optic properties of Siloxane based side chain liquid crystal polymers

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SUMMARYT - *A series of siloxane based side chain liquid polymers have been prepared with a range of molecular weight. For all molecular weight polymers, a smectic phase is observed.*

A marked reduction in T_g, T_{si} as a function of reducing the molecular weight has been observed. Infrared dichroism measurements have been made to determine the order parameters of the liquid crystalline side chain polymers. It was found that the higher the molecular weight of the polymer, the higher the threshold voltage of the electro-optic response, and the lower the order parameter. The increase in the threshold voltage with increasing molecular weight may be related to the intrinsic curvature elasticity and hence to the coupling between mesogenic units and the polymer.

1. Introduction

The design principles of side-chain crystal are well established (Warner, 1989). These molecular composites consist of a flexible polymer backbone and a rigid mesogenic unit joined as a side chain to the polymer backbone by means of a flexible coupling chain. Although there were initial suggestions that the spacer chain would decouple the motion of the mesogenic unit from the polymer backbone, it is now clear that the relatively short length of the coupling chains will result in some interaction between the mesogenic unit from the polymer backbone. The theoretical predictions of Warner et al (1989) and others (Vasilenko *et al*, 1985) have been substantiated by a number of neutron scattering studies (Keller *et al*, 1985; Kirste *et al*, 1985).

In the nematic phase, the coupling in systems based upon methacrylates appears to be negative in the sense that polymer chains lie preferentially perpendicular to the mesogenic units (Keller *et al*, 1985; Kirste *et al*, 1985) in contrast to the parallel arrangement in acrylate based backbones (Mitchell *et al*, 1987). For the smectic phase, the density of the layered structure of the mesogenic units acts to confine the polymer chain to a layer perpendicular to the mesogenic units (Keller *et al,* 1985, Mitchell *et al*, 1987). By a suitable chemical design, polymers can be synthesized, although there is some possibility of interlayer hopping by the polymer chain (Noierz *et al*, 1988; Hardouin *et al*, 1988), that will exhibit the well known electric and magnetic filed effects displayed by low molar mass counterparts (Moussa *et al*, 1987). In such electro-optic effects, what is the role of the polymer backbone? It is clear that the polymeric nature of the liquid crystal phase strongly affects the response times through a highly temperature dependent viscosity. Furthermore the electro–optic response of a side-chain liquid crystal polymer is particularly sensitive to the thermal history of each sample, and this may be related to the coupling of the side–chain organization to the very long relaxation time of the polymer backbone (Killer *et al*, 1985).

In this contribution we focus on the polymer backbone in determining the static properties of the liquids crystal phase. In particular we want to give attention on the influence of the molecular weight upon curvature elasticity, which determines the case with the director pattern

and may be modified using external fields. We shall consider a series of Siloxane based side-chain liquid crystal homopolymers in which the molecular weight is systematically varied. The state of orientational order in these homopolymers is evaluated through the use of infrared spectroscopy which selectively probes only the mesogenic side-chains.

Carefully programmed electro-optic measurements are used to evaluate the relationships between the variation in molecular weight, orientational order and electro– optical properties.

2. Materials

A series of Siloxane based side-chain liquid crystalline homopolymers of the repeat unit shown in the figure have been prepared by free radical polymerization (Kirste, 1985).

(figura senza numero)

The standard conditions used, (initiation by AIBN in chlorobenzene at 55^0C) have been modified to give a range of molecular weight by increasing the initiator concentration and by the addition of various amounts of dodecanethiol (Mitchell *et al*, 1987) as a chain transfer agent (Boffel C. *et al*, 1986). Both these modifications reduce the molecular weight of the polymer produced. The homopolymers are characterized by a smectic phase, identified as smectic A by Davideon *et al* (Mitchell *et al*, 1999), over the greater part of the liquid crystal range. All the phase transitions, Tg and TSi are depressed (Table 1) as has been seen for polyacrylate and polysiloxane based side-chain liquid crystalline polymer systems ((Boffel C. *et al*, 1986).

Table 1
Molecular Weight and Phas

Polymer	M_W	DP_n	$T_g{}^0$ C	$T_{SI}{}^0$ C
1	1.91×10^6	320	50	134
2	7.1×10^5	102	40	129
3	9.1×10^4	15	29	105
4	5.55×10^3	8	18	80
5	2.99×10^3	4	5	66

When interpreting the phase behaviour of these materials we have to be cautious in attributing effects solely to differences in molecular weight: in the lowest molecular weight members of this series a significant percentage of end groups will be chain transfer agent fragments, consisting of a long alkyl chain bound through a sulphur atom.

This percentage has been determined by micro–analysis for the sulphur content of the polymers (Kirste, 1985), and has been found to be 20% for 5 and 14% for 4. In order to ascertain whether the plasticizing effect of the dodecyl chains is responsible for the anomalous

phase behaviour, we prepared a series of copolymers of the liquid crystalline monomer and dodecyl siloxane, under conditions similar to that of polymer 2. These materials showed similar phase behaviour to the homopolymers, in terms of detectable smectic to isotropic phase transitions, even when up to 15 mol % of the non-mesogenic monomer was incorporated. The molecular weight data were determined by G.P.C (RAPRA Ltd) at room temperature in tetraphdrofuran, using a combination of concentration and viscosity detectors and UNICAL universal calibrattion software.

3. Experimental methods

An electro –optic experiment involves the measurement of changes in the optical properties of thin films of the liquid crystal polymers induced through the application of electric fields. The experimental arrangement used for these electro–optic measurements has been described previously in detail elsewhere (Keller *et al*, 1985; Noriez *et al*, 1988). The electro– optic cell (described below) was held inside a temperature controlled stage providing a uniform temperature environment with fluctuations of 0.25^0C. the optical system consisted on a 5 mW helium–neon laser with crossed polarizer and a analyzer system and a photodiode with amplifier for intensity measurements.

Electric fields were provided by means of a power amplifier (Hewlett Packard 6827 A) driven by a function generator (Thunder TG 501). This arrangement provided waveforms in the range 0.05 to 30 KHz with peak to peak voltages in the range 0 to 240 volts. The intensity of the transmitted light through this optical cell was recorded as a function of time using a microcomputer system based around a compatible PC.

Through the use of a specially written software system EOCS, sophisticated electro- optical experiments could be performed on a continuous or cyclic basis involving temperature control, data recording, field switching and analysis (Keller *et al*,1985). The electro–optic cells with predefined director orientation were constructed from patterned thin oxide coated glass slides. After cleaning in an ultrasonic bath and drying, the cell electrodes were coated with a thin layer of a polyimide precursor consisting of a 5% solution of Rodehftal 322 in dimethylformamide using a spin-coater.

These coated slides were heated and tabbed in a single direction with a cloth. A small portion of the selected polymer sample was carefully applied onto one of the treated glass electrodes, which was then heated above its clearing point in order to allow the trapped air to escape. The second glass electrode was then mounted above the first electrode using 0.025 mm thickness Kapton sheet as spacers. The quality of the direction orientation was confirmed through examination with a polarizing microscope. Complete and uniform director alignment was obtained by holding the completed electro-optic cell at a temperature 1C° below the measured clearing point for 15 hours. This technique was successful in inducing a uniform director alignment in elector-optic cells for all the materials used in this work, in all cases, the predefined director alignment was parallel to the electrode surface and to the direction of rubbing. Some cell showed small numbers of defects such – as small loops when examined using the polarizing microscope, however these largely disappeared after holding the cells at elevated temperatures.

The orientational order parameter ‘S’ for each polymer sample at a variety of temperatures was measured using infar-red dichrosim employing a Perkin–Elmer 580 B spectrometer fitted with a wire grid polarizer and heating stage (Noierz *et al.*, 1988). The order parameter measurements were made using monodomain samples prepared as prealigned cells similar to those used for the electro-optic measurements but using crystals of potassium bromide as the cell windows (Noierz *et al.*, 1988)

4. Static electro–optic properties

We have used the experimental arrangement described above to evaluate the static electro-optic properties for each member of the molecular weight series of the side chain liquid crystal polymers shown in Table 1. In these experiments, we determine the minimum or threshold electric field required to distort the surface predefined director orientation. In this geometry, the electric field perturbs an initial planar surface alignment and this mode of deformation is dominated by the splay component of the curvature elasticity K_{11} for small deformations. The threshold voltage is related to the curvature elasticity, assuming strong anchorage by (Moussa *et al.*, 1987):

$$U_{th} = \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta\varepsilon}} \qquad [1]$$

where $\Delta\varepsilon$ is the anisotropy of the dielectric permittivity and U_{th} the threshold voltage. From this equation it can be seen that the evaluation of K_{11} should be straight forward procedure through the measurement of $U_{th.}$, however for a polymer system there are a number of particular problems of evaluating U_{th}, each of which relates to the high viscosity of the polymer. The most important is to ensure that before starting any measurements the sample is in a complete equilibrium state. For each of the samples considered and for each temperature of measurement we have established the real relaxation of the polymer system through use of cyclic electro- optic measurements(Killer *et al.*, 1985; Noriez *et al.*, 1988).

All threshold voltage measurements were made after the sample had been held at the required temperature for a period of time at least three times longer than the relaxation time. As the response time at low voltages is long we determined the threshold voltage from a plot of the change in the transmitted optical intensity as a function of the applied small voltage. By extrapolation this method allowed both the true threshold voltage to be estimated and any dynamic effects to be excluded. To each the steady state between each voltage step the samples were left for about 3-5 hours and this was checked by monitoring the transmitted light versus time.

Typically at each stage the sample was held for period of time ten times longer than the response time. The results obtained for the materials in this study are presented in Fig.1. There is marked reduction in the threshold voltage for both increasing temperature and reducing molecular weight. In this series of polymers, the chemical composition other than the proportion of end-groups, is unchanged and hence, should be unchanged and therefore the observed variations in threshold, voltages must arise as a consequence of the differing degrees of polymerization

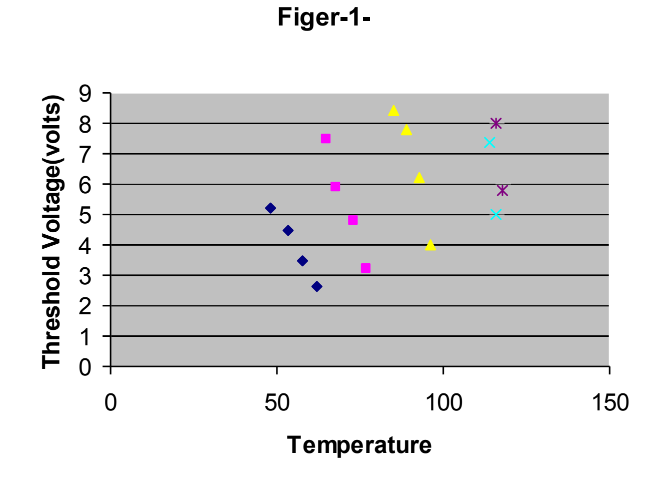


Fig.1
The experimental threshold voltages for a molecular weight series of siloxane based side-chain liquid crystal polymer plotted as a function of temperature.

The symbols refer to the polymer listed in table 1.
Polymer 1 - □, polymer 2 - △ , polymer 3 - ⬭ , polymer 4 - ☆, polymer 5 - ▭

Figure 2 marks a direct comparison of the threshold voltages obtained in the smectic phase at a constant step below T_{NI} for the series of polymers prepared. It is clear that there is an increase in the threshold voltage with increasing molecular weight. Indeed if the effects of the end-groups of the polymer chain are taken into account (these must reduce) then the trend will be even more marked. It is emphasized that any dynamic effects arising from changing viscosity have been eliminated in the procedures outlined above. Few contributions (23,25) have dealt with measuring the threshold voltage for siloxane polymers, unfortunately molecular weight data were not given, however the threshold voltages reported are broadly similar to those found here. The marked increase of the threshold voltage with temperature follows similer trends observed for polyacrylate based materials (Noriez *et al.,* 1988; Renz, 1986). For a smectic phase the value of K_{11} is usually similar to that observed for the nematic phase (Moussa *et al*, 1987) since layer deformation is a relatively facile process.



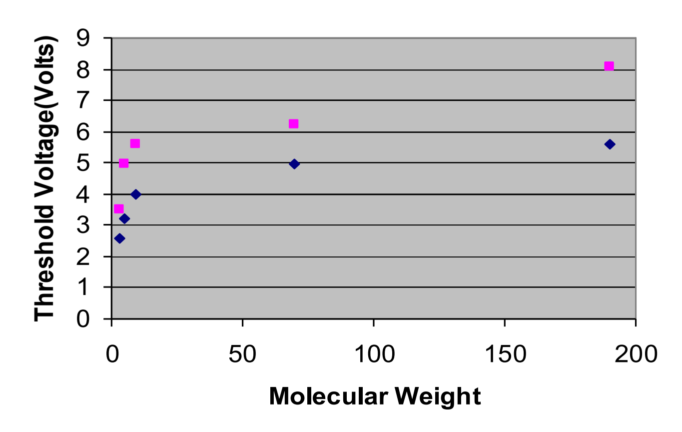


Fig.2
The experimental threshold voltage plotted as a function of molecular weight
for measurements at T_{NI} –T = 1⁰ C (□) and at T_{NI}-T = 3⁰C (◊)
for each of the polymer of the molecular weight series.

5. Order parameters

We have measured the order parameter through the dichroic ratio for the absorption peak at 2235 cm^{-1} which arises from the C ≡N stretching vibration in relation to the predetermined director alignment or rubbing direction. This may be used to define an optical order parameter S which in fact assumes that the absorption moment of the C-N bond is parallel to the long axis of the mesogenic unit (Noriez *et al.*, 1988; Rings Dorf, 1982) this order parameter measures directly the orientational order of the side-chains. Since these polymers exhibits long relaxation times, considerable care was taken to ensure that equilibrium conditions are achieved, hence each sample was held for periods up to 130 hours before the final measurements were performed, although the changes in the dichroic ratio that occurred as a result of temperature steps were usually established within ten hours. Measurements were made for each sample over a range of temperatures, the resultant order parameters are displayed in Fig.3.The variation of the order parameter with temperature for each particular sample shows the classical shape predicted by the Maier and Saupe theory (Ohm *et al.*, 1988).

The variation of the polymer weight leads to distinctive trends in the order parameter versus temperature plots, however each individual curves has the same basic form. From Fig.(3) it is clear that the materials with highest molecular weights exbibit the lowest order parameters and

this effect has also been observed Boeffel et al. (Mitchell *et al* 1991), for some acrylate based side chain polymers. Although it might appear that the lower order parameters at higher molecular weights reflect an incomplete monodomain formation due to the high viscosity, there was no experimental evidence to suggest that the measurements were anything other than true steady state values.

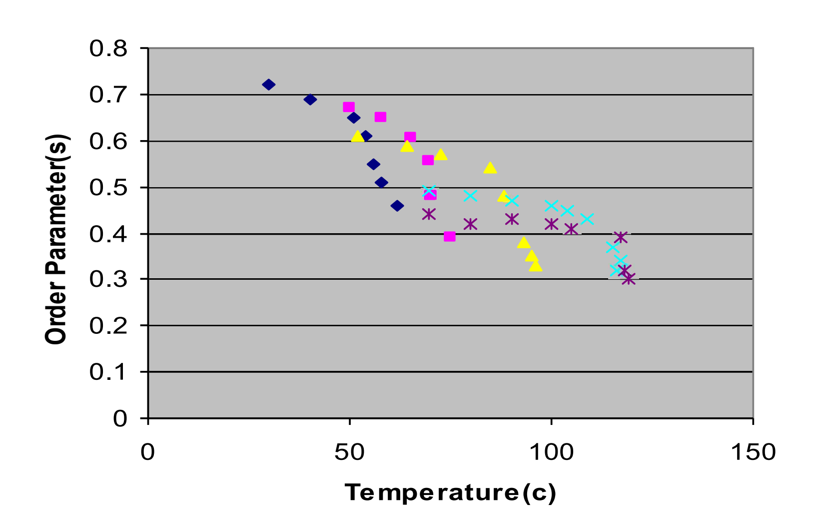


Fig.3
The order parameters S plotted as a function of temperature for the five polymer listed in Table 1. Key as in Fig.1.

The values and temperature dependence of the order parameter observed for polymer 2 closely obtained for an acrylate based material with the same mesogenic unit and the same degree of polymerization(Noierz *et al.*, 1988).

6. Elastic constants

Microscopic models of curvature elasticity in liquid crystal polymers are restricted to the main chain variety and we must fall back on the traditional approach used for non-polymeric liquid crystal system, that of Saupe and Nehring who used the Maier-Saupe mean field theory to established the relationship (Ohm *et al*,. 1988).

[2] $$K_{ii} = \frac{C_{ii} S^2}{V^3 \pi}$$

where C_{ii} is a constant dependent upon molecular properties, and V is the molar volume. This type of relationship predicts that the value of the of elastic constant is expected to be dominated by the order parameters. It also predicts that the splay, twist and bend curvature elastic are equal. However, Eq.[2] does provide a route to illuminate the molecular weight dependence of the threshold voltage. We may combine Eq.[1] and Eq.[2] to give (Noierz *et al.*, 1988):

$$U_{th}^2 \propto S$$

The purpose of the results is to allow the temperature order parameter variations on K_{ii} to be considered independently of the effect of those variables on the dielectric properties. Fig.4 shows the variation of the U^2_{th} with the order parameter S for each of the polymers considered in this study. From the experimental data a clear trend appears between the threshold voltage

and the order parameter. but any reasonable fit to the data allowing the curve to pass through $U_{th} = S = 0$, would require a non-linear relationship at variance with the general prediction described above.

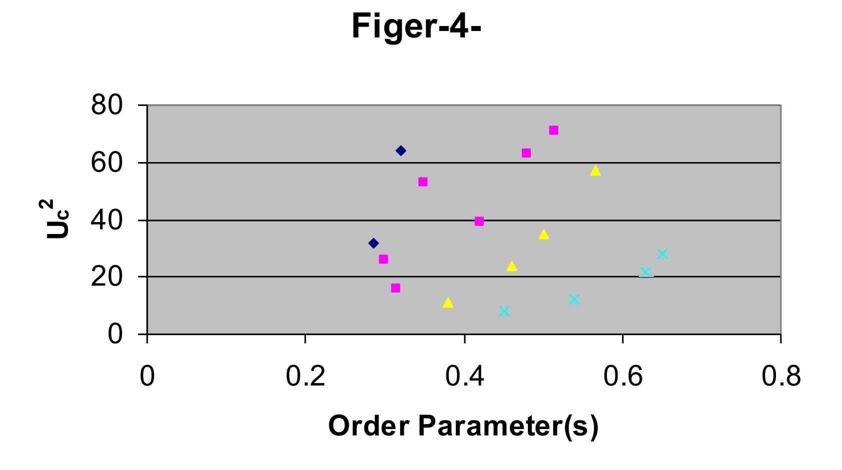


Fig.4
A plot of the square of the measured threshold voltage against the order parameter at the temperature of measurement for each of the five siloxane based polymer. Key as in Fig.1.

The fact that the experimental data suggests a complicated relationship between deformation and the level of order involving terms other than S is perhaps hardly surprising. Fig.4 shows that even when the variation in order parameters is taken into account there remain substantial differences between the different members of this molecular weight series. In other words, if the increasing of the threshold voltage as a function of molecular weight, as shown in Fig.2, was due to a reduction in the order parameter along, then all five curves in Fig.4 would superimpose. This is not the case and we can relate the differences in the slope of these curves to the temperature independent coefficients *C* which are clearly affected by the molecular weight.

The variation in slope indicates that there a is strong coupling between the mesogenic side groups and the polymer chain plays a significant part even in the static electro– optic properties. The curvature for the plots in Fig.4 is similar to that observed for studies of polycrylate based polymers (Noierz *et al.*, 1988), and indicates that this higher order dependence is a more general feature.

7. Discussion

Variation of the degree of polymerization in this series of siloxane based side- chain liquid crystal polymers has impact upon the phase behavior, the order parameter and upon the electro-optic properties. It is found that decreasing the molecular weight lowers the phase transition temperatures. Complementary to the reduction of the phase transition temperature with decreasing the molecular weight of the polymers there is a marked lowering of the glass transition temperature. It is clear that increasing the molecular weight will not change the magnitude of dielectric anisotropy and hence if the curvature elastic constant is unaffected by the degree of polymerization the threshold voltage should be constant. The observation that U_{th} increases with increasing molecular weight indicates an increase in the elastic contant *K*.

We may attribute the increase of the intrinsic elastic constant with molecular weight to changing levels of interaction between the mesogenic units and the polymer backbone. There is evidence for this from samll angle neutron scattering experiments carried out by (Mitchell *et al.,* 1987; Al-Ammar *et al.,* 1992) on different molecular weight methylsiloxane based polymer. They found that the anisotropy of the radius of gyration by 30-40% on an approximate doubling of the

molecular weight. It is possible to divide the contribution of the polymer chain to the apparent curvature elasticity into two components. The first arises from the elasticity of interactions between the chains as might arise from entanglements. Such effects have been observed in the electro optic properties of cross–linked side–chain liquid crystal polymers (Noierz *et al.*, 1988; Hardouin, 1988) and the increase in threshold voltage was substantial. It would perhaps be expected that the threshold voltage would be much lower when the molecular weight falls below that critical weight required for entanglements and this additional elasticity would increase with increasing temperature. The second contribution arises more directly from the coupling of the mesogenic units to the polymer backbone and is perhaps typified by the increase in the threshold voltage which arises as the coupling chain is shortened (Moussa *et. al.*). It is not clear here which is the dominant factor.

8. Conclusion

This study is focused on the properties of a series of polymer with differing molecular weight based on the siloxane backbone. It is found that reducing the molecular weight lowers the phase transition and eventually leads to a distabilisation of the smectic phase. The effect of reducing the molecular weight of the polymer is to lower the observed voltage. This may be related to an increase in the intrinsic constant of the liquid crystal polymer. It is found that there is a strong coupling between the mesogenic side chain groups and the polymer chain and that the elasticity of the polymer chain plays a strong part even in the static elector-optic properties. The orientational order of the mesogenic units follows a similar temperature dependence for each of the differing polymer molecular weight, although the magnitude of the order parameter is much reduced as the molecular weight increase.

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